Preface

This thesis presents results of investigations on fields and multipole expansion coefficients in axially symmetric (referred to as 3D) and two dimensional (2D) ion trap mass analysers. 3D mass analysers have a three-electrode geometry with two (electrically shorted) endcap electrodes and one central ring electrode. rf-only or rf/dc potential applied across the electrodes creates a linear trapping field in the central cavity of the mass analyser. 2D mass analysers have four longitudinal electrodes in which the opposite pairs of electrodes are electrically shorted. Here, rf-only or rf/dc potential applied across the pair of electrodes creates a linear trapping field and fragment ions of the analyte gas are trapped along the central axis of the mass analyser. Both these mass analysers have apertures machined on the electrodes (holes in case of 3D traps and slits in case of 2D traps) to permit entry of electrons for ionising the analyte gas and for collection of destabilized fragment ions. This thesis is concerned with how these apertures influence the fields and multipole expansion coefficients within the traps.

This thesis is divided into five chapters.

Chapter 1 provides the background information which is required for the thesis. It begins with a description of the geometry of the 3D and the 2D mass analysers used in the present work. These include the quadrupole ion trap (QIT) and cylindrical ion trap (CIT) for 3D structures and the linear ion trap (LIT) and the rectilinear ion trap (RIT) for 2D structures. This is followed by a brief description of the numerical method, the boundary element method (BEM), used in the thesis. Also presented here are the Green's function for 3D and 2D geometries. In the final section, the scope of the thesis is presented.

Chapter 2 presents two approximate analytical expressions for nonlinear electric fields in the principal direction in axially symmetric (3D) and two dimensional (2D) ion trap mass analysers with apertures on the electrodes. Considered together (3D and 2D), we present composite approximations for the principal unidirectional nonlinear electric fields in these ion traps.

The composite electric field E has the form

$$E = E_{\text{noAperture}} + E_{\text{dueToAperture}}$$

where $E_{\text{noAperture}}$ is the field within an imagined trap which is identical to the practical trap except that the apertures are missing; and where $E_{\text{dueToAperture}}$ is the field contribution due to apertures on the two trap electrodes. The field along the principal axis of the trap can in this way be well approximated for any aperture that is not too large.

To derive $E_{\text{dueToAperture}}$, classical results of electrostatics have been extended to electrodes with finite thickness and different aperture shapes.

$E_{\text{noAperture}}$ is a modified truncated multipole expansion for the imagined trap with no aperture. The first several terms in the multipole expansion are in principle exact (though numerically determined using the BEM), while the last term is chosen to match the field at the electrode. This expansion, once computed, works with any aperture in the practical trap.

The composite field approximation for axially symmetric (3D) traps is checked for three geometries: the quadrupole ion trap (QIT), the cylindrical ion trap (CIT) and an arbitrary other trap. The approximation for 2D traps is verified using two geometries: the linear ion trap (LIT) and the rectilinear ion trap (RIT). In each case, for two aperture sizes (10% and 50% of the trap dimension), highly satisfactory fits are obtained. These composite approximations may be used in more detailed nonlinear ion dynamics studies than have been hitherto attempted.

In Chapter 3 we complement and complete the work presented in Chapter 2 by considering off-axis fields in the axially symmetric (3D) and the two dimensional (2D) ion traps whose electrodes have apertures. Our approximation has two parts. The first, $E_{\text{noAperture}}$, is the field obtained numerically for the trap under study with no apertures. We have used the boundary element method (BEM) for obtaining this field. The second part, $E_{\text{dueToAperture}}$, is an analytical expression for the field contribution of the aperture.

In $E_{\text{dueToAperture}}$, aperture size is a free parameter. A key element in our approximation is the electrostatic field near an infinite thin plate with an aperture, and with different constant valued far field intensities on either side. Compact expressions for this field can be found using separation of variables, wherein the choice of coordinate system is crucial. This field is, in turn, used four times within our trap specific approximation.

The off-axis field expressions for the 3D geometries were tested on the quadrupole ion trap (QIT) and the cylindrical ion trap (CIT), and the corresponding expressions for the

2D geometries were tested on the linear ion trap (LIT) and rectilinear ion trap (RIT). For each geometry, we have considered apertures which are 10%, 30% and 50% of the trap dimension. We have found that our analytical correction term $E_{\text{dueToAperture}}$, though based on a classical small-aperture approximation, gives good results even for relatively large apertures.

Chapter 4 presents approximate analytical expressions for estimating the variation in multipole expansion coefficients with the size of apertures in axially symmetric (3D) and two dimensional (2D) ion trap mass analysers. Following the approach adopted in Chapter 2 and Chapter 3 which focused on the role of apertures to fields within traps, here too, the analytical expression is a sum of two terms, $A_{n,\text{noAperture}}$, the multipole expansion coefficient for a trap with no apertures and $A_{n,\text{dueToAperture}}$, the multipole expansion coefficient contributed by the aperture. $A_{n,\text{noAperture}}$ has been obtained numerically and $A_{n,\text{dueToAperture}}$ is obtained from the n^{th} derivative of the potential within the trap.

The expressions derived have been tested on two 3D geometries and two 2D geometries. These include the quadrupole ion trap (QIT) and the cylindrical ion trap (CIT) for 3D geometries and the linear ion trap (LIT) and the rectilinear ion trap (RIT) for the 2D geometries. Multipole expansion coefficients A_2 to A_{24}, estimated by our analytical expressions were compared with the values obtained numerically (using the boundary element method) for aperture sizes varying up to 50% of the trap size.

In all the plots presented, it is observed that our analytical expression for the variation of multipole expansion coefficients versus aperture size closely follows the trend of the numerical evaluations for the range of aperture sizes considered. The maximum relative percentage errors, which provide an estimate of the deviation of our values from those obtained numerically for each multipole expansion coefficient, are seen to be in the range of 10% to 15%. The leading multipole expansion coefficient, A_2, however, is seen to be estimated very well by our expressions, with most values being within 1% of the numerically determined values, with larger deviations seen for the QIT and LIT only at larger aperture sizes.

Chapter 5 presents a few concluding remarks.